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Molecular Engineering for Mechanically Resilient and Stretchable Electronic Polymers and Composites

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Molecular Engineering for Mechanically Resilient and
Stretchable Electronic Polymers and Composites

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Abstract

In the three-year project supported by the AFOSR Young Investigator Program, my research laboratory published 24 papers. This final report summarizes the key results in the final year of funding. As described in the original proposal document, the first goal of this project was to establish the design criteria for introducing elasticity and ductility in high-performance conjugated (semiconducting) polymers and polymer-small molecule composites by a rigorous analysis of the structural determinants of the mechanical properties of this type of material. To this end, we developed coarse-grained molecular dynamics simulations that successfully predicted the mechanical properties of conjugated polymers and polymer-fullerene composites (Root et al. *Macromolecules* **2016**, *49*, 2886-2894). In collaboration with Prof. Frederik Krebs at the Danish Technical University, we elucidated the mechanical properties of a large library of >50 low-bandgap semiconducting polymers to determine molecular design rules for maximizing electronic performance with good mechanical deformability (Roth et al. *Chem. Mater.* **2016**, *28*, 2363-2373). We also determined the effect of cyclic stretching on the microstructure and mechanical properties of conjugated polymers (Printz et al. *Synth. Met.* **2016**, *217*, 144-151). We used many of these results to produce a new type of ultra-thin, skin-wearable solar cell that could survive many cycles of deformation without degrading significantly (O'Connor et al. *Sol. Energy Mater. Sol. Cells* **2016**, *144*, 438-444). Complementary to the molecular approaches for improving the mechanical robustness of stretchable organic electronics, we also explored the role of encapsulation and adhesion in electronic devices and found that a large increase in stretchability is possible with the use of a stretchable encapsulating layer (Sawyer et al. *Extreme Mech. Lett.* **2016**, doi:10.1016/j.eml.2016.03.012). In addition to polymers, we explored the stretchability of semiconducting small molecules, in collaboration with Profs. Quyen Nguyen and Guillermo Bazan (Rodriquez et al. *ACS Appl. Mater. Interfaces* **2016**, *8*, 11649-11657). We reviewed our results in the context of wearable power sources in an invited book chapter (O'Connor et al. "Soft power: Stretchable and ultra-flexible energy sources for wearable and implantable devices" in *Stretchable Bioelectronics for Medical Devices and Systems*, J.A. Rogers, D.H. Kim, and R. Ghaffari, Eds. Springer, 2016). We also performed an analysis of the interplay and perceived competition between charge-transport and mechanical deformability in organic semiconductors in an invited review (Printz et al. *Appl. Phys. Rev.* **2016**, *3*, 021302). In an invited perspective article, I described nomenclature and metrology in the field of stretchable electronics (Lipomi *Adv. Mater.* **2016** DOI: 10.1002/adma.201504196).

1. Predicting the Mechanical Properties of Organic Semiconductors Using Coarse-Grained Molecular Dynamics Simulations

The ability to predict the mechanical properties of organic semiconductors is of critical importance for roll-to-roll production and thermomechanical reliability of organic electronic devices. Here, we describe the use of coarse-grained molecular dynamics simulations to predict the density, tensile modulus, Poisson ratio, and glass transition temperature for poly(3-hexylthiophene) (P3HT) and its blend with C₆₀. In particular, we show that the resolution of the coarse-grained model has a strong effect on the predicted properties. We find that a one-site model, in which each 3-hexylthiophene unit is represented by one coarse-grained bead, predicts significantly inaccurate values of density and tensile modulus. In contrast, a three-site model, with one coarse-grained bead for the thiophene ring and two for the hexyl chain, predicts values

that are very close to experimental measurements (density = 0.955 g cm^{-3} , tensile modulus = 1.23 GPa , Poisson ratio = 0.35 , and glass transition temperature = 290 K). The model also correctly predicts the strain-induced alignment of chain, as well as the vitrification of P3HT by C_{60} and the corresponding increase in the tensile modulus (tensile modulus = 1.92 GPa , glass transition temperature = 310 K). Although extension of the model to poly(3-alkylthiophenes) (P3ATs) containing side chains longer than hexyl groups—nonyl (N) and dodecyl (DD) groups—correctly predicts the trend of decreasing modulus with increasing length of the side chain measured experimentally, obtaining absolute agreement for P3NT and P3DDT could not be accomplished by a straightforward extension of the three-site coarse-grained model, indicating limited transferability of such models. Nevertheless, the accurate values obtained for P3HT and P3HT: C_{60} blends suggest that coarse graining is a valuable approach for predicting the thermomechanical properties of organic semiconductors of similar or more complex architectures. This paragraph was adapted from our paper Root et al. *Macromolecules* **2016**, *49*, 2886-2894.

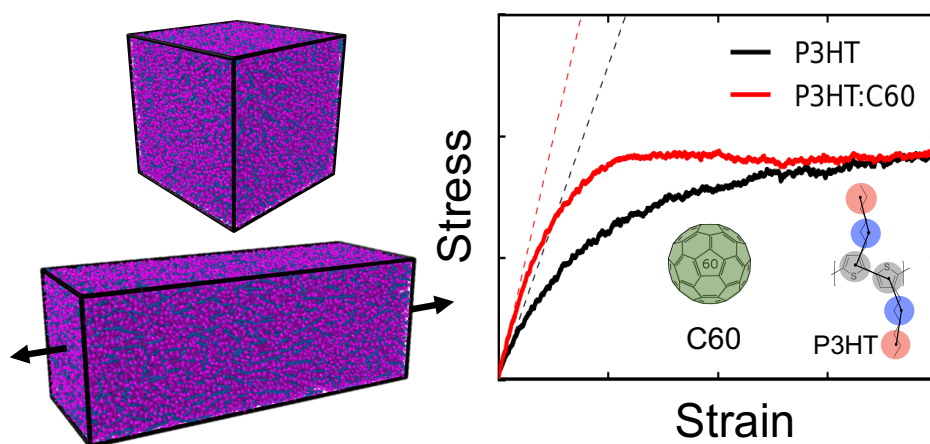


Figure 1. Visualization of coarse-grained molecular dynamics simulations on polymer:fullerene bulk heterojunction films. The plot shows the stiffening of C_{60} fullerene (anti-plasticization) on the mechanical properties of P3HT simulated with a three-site coarse-grained model.

2. Mechanical Properties of a Library of Low-Bandgap Polymers

The mechanical properties of low-bandgap polymers are important for the long-term survivability of roll-to-roll processed organic electronic devices. Such devices—e.g., solar cells, displays, and thin-film transistors—must survive the rigors of roll-to-roll coating and also thermal and mechanical forces in the outdoor environment and in stretchable and ultra-flexible form factors. This paper measures the stiffness (tensile modulus), ductility (crack-onset strain), or both, of a combinatorial library of 51 low-bandgap polymers. The purpose of this study is to systematically screen a library of low-bandgap polymers to better understand the connection between molecular structures and mechanical properties, in order to design conjugated polymers that permit mechanical robustness and even extreme deformability. While one of the principal conclusions of these experiments is that the structure of an isolated molecule only partially

determines the mechanical properties—another important co-determinant is the packing structure—some general trends can be identified. (1) Fused rings tend to increase the modulus and decrease the ductility. (2) Branched side chains have the opposite effect. Despite the rigidity of the molecular structure, the most deformable films can be surprisingly compliant (modulus ≥ 150 MPa) and ductile (crack-onset strain $\leq 68\%$). This paper concludes by proposing a new composite merit factor that combines the power conversion efficiency in a fully solution processed device obtained via roll and roll-to-roll coating and printing (as measured in an earlier paper) and the mechanical deformability toward the goal of producing modules that are both efficient and mechanically stable. This paragraph was adapted from our paper Roth et al. *Chem. Mater.* **2016**, 28, 2363-2373.

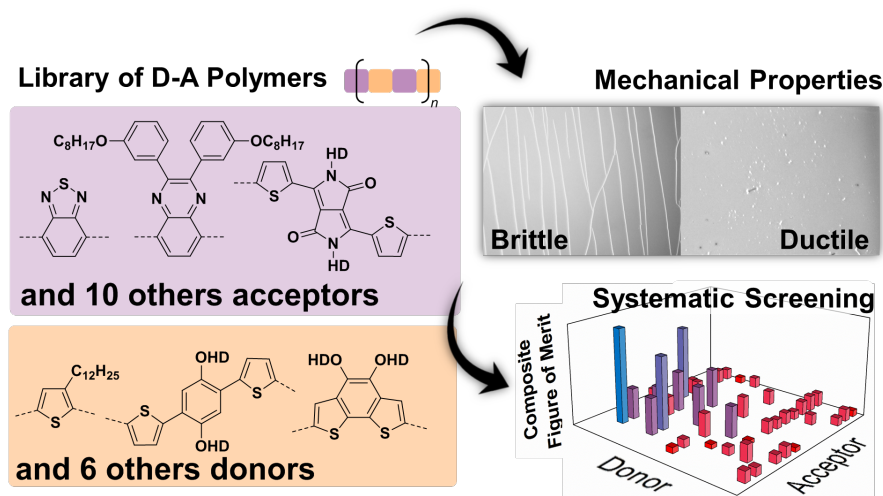


Figure 2. Schematic drawing indicating a library of donor-acceptor low-bandgap conjugated polymers comprising 13 different acceptors and 9 different donors. The mechanical properties were measured and the structural determinants of stiffness and brittleness were elucidated.

3. Fatigue in organic semiconductors: Spectroscopic evolution of microstructure due to cyclic loading in poly(3-heptylthiophene)

Organic electronic materials have many characteristics that make them attractive for mechanically deformable—i.e., flexible and stretchable—applications. While deformation often degrades the performance of these devices, very little is known about the effects of cyclic loading—i.e., mechanical fatigue—on the microstructure and mechanical properties of the active materials. This paper examines the evolution of microstructure and stiffness of thin films of poly(3-heptylthiophene) (P3HpT) as the film undergoes cyclic straining using ultraviolet-visible (UV-vis) spectroscopy and the mechanical buckling technique. Thin films of P3HpT are cyclically stretched by 5, 10, or 25 percent (i.e., below, at, and above the yield point—the point at which the polymer plastically deforms with strain) up to 10000 cycles. UV-vis absorption spectroscopy is taken in intervals and the weakly interacting H-aggregate model is used to determine the aggregate quantity (from the vibronic progression) and quality (from the exciton bandwidth) in the films. Films cyclically strained at 5 and 10 percent (below and at the yield point) do not undergo significant reduction in the aggregated fraction of polymer chains, while films strained to 25% (above the yield point) undergo a reduction in aggregated fraction of over 10% by the 2000th cycle. At 25% strain, a significant reduction in the buckling wavelength from

$3.4 \pm 0.4 \text{ }\mu\text{m}$ to $2.4 \pm 0.3 \text{ }\mu\text{m}$ is observed within the first 100 strain cycles suggesting a significant reduction in the stiffness and resilience of the films. A significant decrease in ductility is observed in films cyclically strained, and the effect is found to increase with increasing levels of strain. These results suggest that materials cyclically strained below their yield point will retain a microstructure that is their most electronically favorable, and that the mechanical properties of materials strained above their yield point will evolve significantly under repeated deformation. This information can be used to inform design where accommodation of repetitive strain is required, such as outdoor, portable, and wearable devices. This paragraph was adapted from our paper Printz et al. *Synth. Met.* **2016**, 217, 144-151.

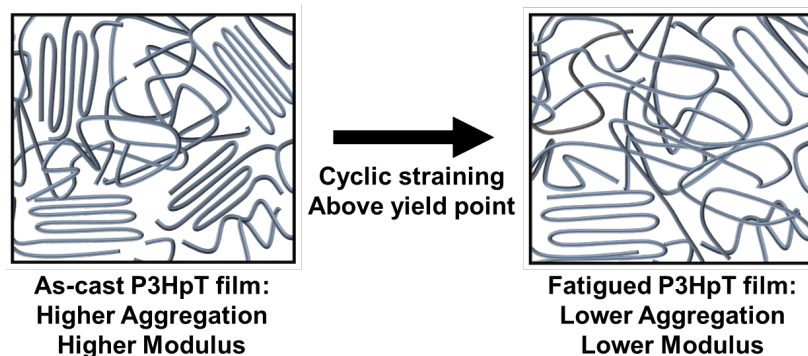


Figure 3. Schematic drawings indicating the hypothesized microstructures of as-cast and fatigued films of poly(3-heptylthiophene) (P3HpT).

4. Wearable organic solar cells with high cyclic bending stability: Materials selection criteria

Despite the intrinsic flexibility of organic electronic materials due to their thinness, a deliberate selection of materials on the basis of their mechanical—not just charge-transport—properties is required for applications with mechanically demanding form factors, such as exist in the field of wearable electronics. This paper describes a skin-wearable solar cell enabled by the deliberate selection or intentional plasticization of the components to enable an extreme level of stability under cyclic bending deformations. In particular, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) films plasticized with 10 percent fluorosurfactant are used for both the anode and cathode, with the cathode layer further modified with polyethyleneimine (PEI) to lower the work function. Use of poly(3-heptylthiophene) (P3HpT) instead of the far more common poly(3-hexylthiophene) (P3HT) as the electron donor permitted extreme deformation because of its increased mechanical compliance (owing to its low glass transition temperature). Cells fabricated on 13- μm polyimide tape and adhered to human skin show stable performance when compressively strained by approximately 75 percent. These compressive strains produce convex and concave buckles with minimum radii of curvature of ca. 100 μm . Finite-element modeling predicts that the films require the ability to withstand a range of strains of 10 percent, when both convex and concave bends are considered. These devices, enabled by the stretchable semiconductor P3HpT, withstand up to one thousand cycles of compression with less than 20 percent degradation in power conversion efficiency, whereas devices based on P3HT show greater degradation after only five cycles, and fail catastrophically

by fifty cycles. The usefulness of the wearable solar cells is demonstrated by their abilities to power an LED and a digital watch. This paragraph was adapted from our paper O'Connor et al. *Sol. Energy Mater. Sol. Cells* **2016**, 144, 438-444.

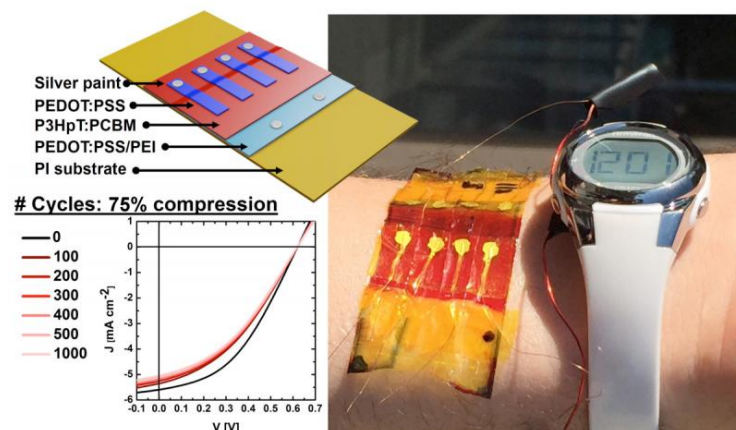


Figure 4. Schematic drawing of a skin-wearable solar cell comprising mechanically robust components. The cells survive significant cyclic loading of at least 1000 cycles of compressive strain. The cells can be worn on the skin and can power wearable devices in natural sunlight.

5. Large Increase in Stretchability of Organic Electronic Materials by Encapsulation

This paper describes a large increase in the stretchability—i.e., resistance to cracking under tensile deformation—of organic semiconductor films produced by encapsulation. Specifically, encapsulation is shown to greatly suppress crack formation and growth in films of materials relevant to organic solar cells. Encapsulated films of the organic bulk heterojunction blend of poly(3-heptylthiophene) and phenyl-C₆₁-butyric acid methyl ester (P3HpT:PCBM) exhibit greater crack-onset strain, lower crack density, and lower average crack length than unencapsulated films. Films of P3HpT:PCBM on polyurethane (PU) showed cracks at $6.6 \pm 0.5\%$ without encapsulation and $40 \pm 4\%$ with encapsulation. Films of the conductive polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) also demonstrate suppressed cracking when encapsulated, as well as reduced dependence of resistance on strain after the crack-onset strain (which indicates a greater useable range of strain for encapsulated vs. unencapsulated films). A finite element model is used to explain the mechanism suppressing crack growth, which involves delocalization of strain around minor defects in the films by the encapsulating substrate. In addition, encapsulation is used to enable the first encapsulated solar cell in which every component is intrinsically stretchable. These cells are stretchable to 9-10% strain, with some cells performing well even after their crack-onset strain of 8-9%, whereas unencapsulated cells fail at 4% strain. This work highlights the necessity to consider encapsulation—already important for protecting the electronically active components of a device from abrasion, weathering, or chemical damage—as an important factor in the mechanical robustness of stretchable devices. This paragraph was adapted from our paper Sawyer et al. *Extreme Mech. Lett.* **2016**, doi:10.1016/j.eml.2016.03.012

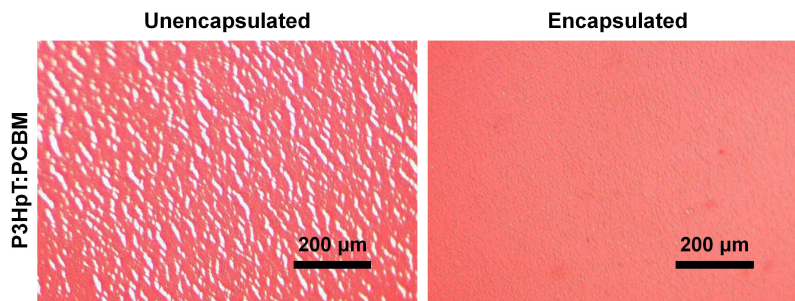


Figure 5. Optical micrographs illustrating the suppression of cracking in P3HPT:PCBM films under 50% tensile strain when unencapsulated (left) vs. encapsulated (right).

6. Mechanical Properties of Solution-Processed Small-Molecule Semiconductor Films

Advantages of semiconducting small molecules—as opposed to semiconducting polymers—include synthetic simplicity, monodispersity, low cost, and ease of purification. One purported disadvantage of small-molecule films is reduced mechanical robustness. This paper measures the tensile modulus and crack-onset strain for pure films of the high-performance solution-processable small-molecule donors 7,7'-[4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b']dithiophene-2,6-diyl]bis[6-fluoro-4-(5'-hexyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole] (DTS(FBTTh₂)₂), 2,5-di-(2-ethylhexyl)-3,6-bis-(5''-n-hexyl-[2,2',5',2'']terthiophen-5-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (SMDPPEH), and 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene), the acceptor 5,5'-(2,1,3-benzothiadiazole-4,7-diyl)-2,1-ethenediylbis[2-hexyl-1H-isoindole-1,3(2H)-dione] (HPI-BT), blends of DTS(FBTTh₂)₂ and SMDPPEH with [6,6]-phenyl C₇₁ butyric acid methyl ester (PC₇₁BM) and with HPI-BT, and bulk heterojunction films processed with the additives 1,8-diiodooctane (DIO) and polystyrene (PS). The most deformable films of solution-processed organic semiconductors are found to exhibit tensile moduli and crack-onset strains comparable to those measured for conjugated polymers. For example, the tensile modulus of as-cast DTS(FBTTh₂)₂ is 0.68 GPa (i.e., comparable to poly(3-hexylthiophene) (P3HT), the common polymer), while it exhibits no cracks when stretched on an elastomeric substrate until strains of 14%. While this high degree of stretchability is lost upon the addition of PC₇₁BM (4.2 GPa, 1.42%), it can be partially recovered using processing additives. Tensile modulus and crack-onset strain are highly correlated, which is typical of van der Waals solids. Increased surface roughness was correlated to increased modulus and brittleness within films of similar composition. Increased elasticity can be rationalized by the presence of alkyl side chains, which decrease the van der Waals attraction between molecules in the crystalline grains. These measurements and observations could have important consequences for the stability of devices based on molecular semiconductors, especially those destined for stretchable or ultra-flexible applications, or those demanding mechanical robustness during roll-to-roll fabrication or use in the outdoor environment. This paragraph was adapted from our paper Rodriguez et al. *ACS Appl. Mater. Interfaces* **2016**, 8, 11649-11657.

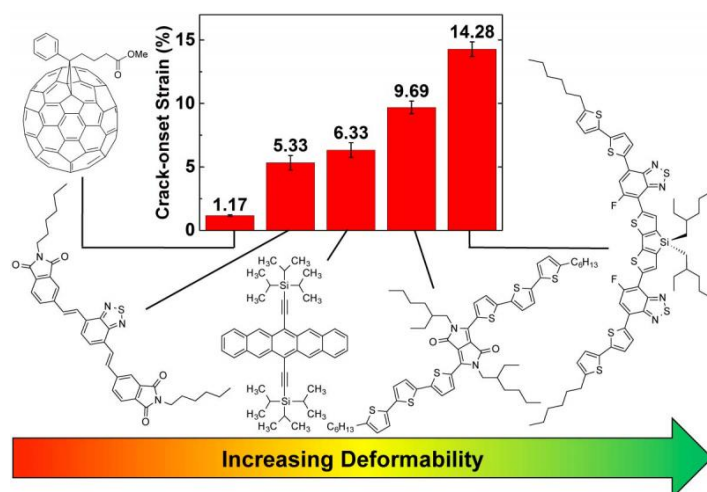


Figure 6. Ductility (i.e., crack-onset strain) of small-molecule semiconductors tested in this project. While the toughness and resilience of these materials are not high, the films show a surprising resistance to cracking.

7. Competition between deformability and charge transport in semiconducting polymers for flexible and stretchable electronics

The primary goal of the field concerned with organic semiconductors is to produce devices with performance approaching that of silicon electronics, but with the deformability—flexibility and stretchability—of conventional plastics. However, an inherent competition between deformability and charge transport has long been observed in these materials, and achieving the extreme (or even moderate) deformability implied by the word “plastic” concurrently with high charge transport may be elusive. This competition arises because the properties needed for high carrier mobilities—*e.g.*, rigid chains in π -conjugated polymers and high degrees of crystallinity in the solid state—are antithetical to deformability. On the device scale, this competition can lead to low-performance yet mechanically robust devices, or high-performance devices that fail catastrophically (*e.g.*, cracking, cohesive failure, and delamination) under strain. There are, however, some observations that contradict the notion of the mutual exclusivity of electronic and mechanical performance. These observations suggest that this problem may not be a fundamental trade-off, but rather an inconvenience that may be negotiated by a logical selection of materials and processing conditions. For example, the selection of the poly(3-alkylthiophene) with a critical side-chain length—poly(3-heptylthiophene) ($n = 7$)—marries the high deformability of poly(3-octylthiophene) ($n = 8$) with the high electronic performance (as manifested in photovoltaic efficiency) of poly(3-hexylthiophene) ($n = 6$). This review explores the relationship between deformability and charge transport in organic semiconductors. The principal conclusions are that reducing the competition between these two parameters is in fact possible, with two demonstrated routes being: (1) incorporation of softer, insulating material into a stiffer, semiconducting material and (2) increasing disorder in a highly ordered film, but not enough to disrupt charge transport pathways. The aim of this review is to provide a bridge between the fields interested in electronic properties and mechanical properties of conjugated polymers. We provide a high-level introduction to some of the important electronic and mechanical properties and measurement techniques for organic electronic devices, demonstrate an apparent competition

between good electronic performance and mechanical deformability, and highlight potential strategies for overcoming this undesirable competition. A marriage of these two fields would allow for rational design of materials for applications requiring large-area, low-cost, printable devices that are ultra-flexible or stretchable, such as organic photovoltaic devices and wearable, conformable, or implantable sensors. This paragraph was adapted from our paper Printz et al. *Appl. Phys. Rev.* **2016**, 3, 021302.

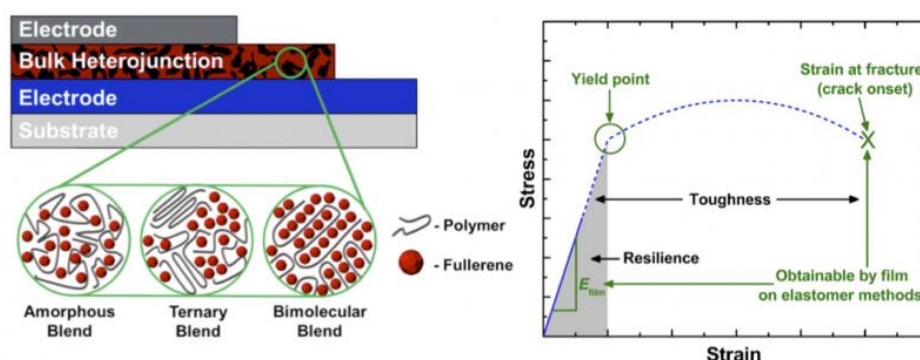


Figure 7. Schematic diagram of an organic bulk heterojunction cell (left) and reconstructed stress-strain curve for conjugated polymers inferred from values obtained by film-on-elastomer methods.

8. Soft Power: Stretchable and Ultra-Flexible Energy Sources for Wearable and Implantable Devices

The development of ultra-compliant power sources is prerequisite to the realization of imperceptible biomedical systems destined to be worn or implanted in the human body. This chapter assesses the viability of conformal piezo- and triboelectric, thermoelectric, and photovoltaic technologies as power sources for biomedical applications. It begins by identifying the amount of energy available to each these modes of power conversion and then gives a brief overview on the methods of fabricating stretchable electronic devices using deterministic structures, random composites, or molecularly stretchable electronic materials. It then provides a detailed description of innovations in “soft power,” where the mentioned design techniques have been employed to develop mechanically compliant power scavengers amenable to integration with stretchable medical devices. The chapter concludes with an analysis of system level power requirements and application specific compatibility, the result of which identifies piezoelectrics and triboelectrics as well suited for intermittent and implantable devices, such as low power pacemakers for piezoelectrics or higher power wearables and neural stimulators for triboelectrics. Thermoelectrics are highly compatible with epidermal and wearable applications, and can be used as a consistent source of power for tattoo chemical or heat sensors, and photovoltaics can generate large amounts of power in full sun, for high power applications like cochlear implants, or less energy in diffuse or ambient light, for powering hearing aids. This paragraph was adapted from our book chapter O’Connor et al. “Soft power: Stretchable and ultra-flexible energy sources for wearable and implantable devices” in *Stretchable Bioelectronics for Medical Devices and Systems*, J.A. Rogers, D.H. Kim, and R. Ghaffari, Eds. Springer, 2016.

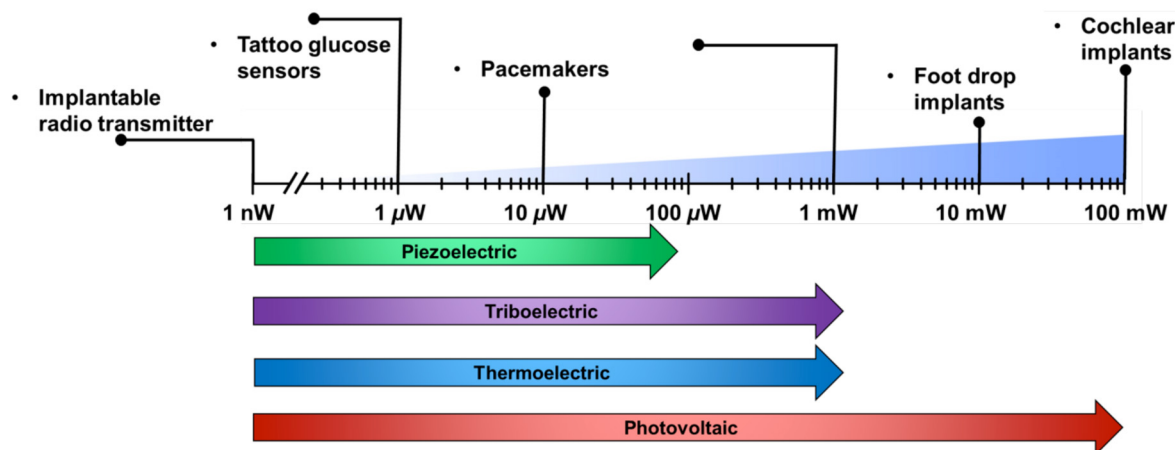


Figure 8. Order of magnitude of typical power consumption of biomedical devices and the range of power generation by the four technologies outlined in this chapter.

9. Stretchable Figures of Merit in Deformable Electronics

Readers of this Special Issue are well aware of the advantages of electronic materials and devices exhibiting the unusual property of “stretchability.” For example, such devices can be bonded to substrates exhibiting complex topography without becoming wrinkled, they are—or should be—resilient and tough, and are enabling the next generation of semiconductor devices in fields as disparate as energy conversion and storage, digital imaging, and implantable biomedical devices. The proliferation of materials, device layouts, and applications in the burgeoning field of stretchable electronics, however, has produced fuzziness in the meaning of the word “stretchable.” A rubber band is stretchable because it exhibits an elastic (reversible) mechanical response over a wide range of imposed strains. In a different sense of the word, no one would object to the classification of chewing gum as stretchable, but its deformation becomes plastic (irreversible) after only a few percent strain. Indeed, visitors to Italy’s *Museo della Tortura* will find The Rack, along with a placard describing its operation and its special place in the depths of medieval sadism, which proved that the stretchability of *Homo sapiens* is not reversible. Stretchability is, nevertheless, a useful word for illustrating the distinction of materials and devices that can be deformed by more than a few percent (while retaining their function) from materials and devices that are only flexible due to the fact that they are thin. Stretchable materials and devices, however, can be made to accommodate strain using several different strategies, which are based on using either composite materials or electronic materials that are stretchable in the bulk. This paragraph was adapted from our paper Lipomi *Adv. Mater.* **2016** DOI: 10.1002/adma.201504196

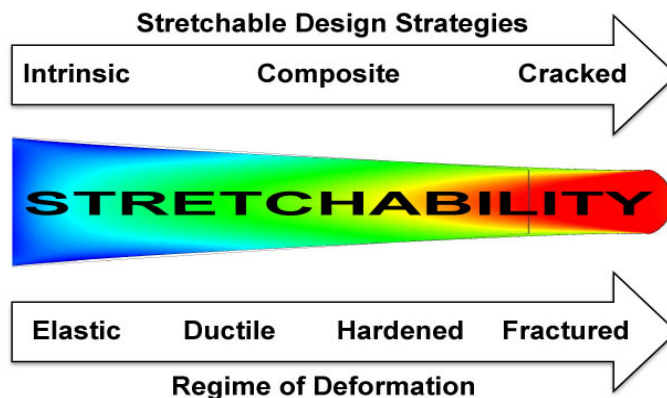


Figure 9. Conceptual drawing showing stretchable design strategies and regimes of deformation that allow increasing deformation with retention of function.

10. Next steps

In the first and second years of funding, we have established many of the design criteria for semiconducting polymers that exhibit both high tensile elasticity and good photovoltaic behavior. In the final year of funding and beyond, we will explore new molecular architectures that exhibit extreme elasticity. Implicit in this goal is to gather fundamental insights into the ways in which mechanical softness can coexist with state-of-the-art charge-transport properties in a single material. In particular, we are exploring how to increase the charge-transport performance of stretchable organic semiconductors so that it is possible to obtain truly excellent devices with intrinsic or molecular stretchability.

1.

1. Report Type

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Electronic Polymers and Composites**Grant/Contract Number****AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".**

FA9550-13-1-0156

Principal Investigator Name**The full name of the principal investigator on the grant or contract.**

Darren J Lipomi

Program Manager**The AFOSR Program Manager currently assigned to the award**

Charles Lee

Reporting Period Start Date

04/01/2013

Reporting Period End Date

03/31/2016

Abstract

In the three-year project supported by the AFOSR Young Investigator Program, my research laboratory published 24 papers. This final report summarizes the key results in the final year of funding. As described in the original proposal document, the first goal of this project was to establish the design criteria for introducing elasticity and ductility in high-performance conjugated (semiconducting) polymers and polymer-small molecule composites by a rigorous analysis of the structural determinants of the mechanical properties of this type of material. To this end, we developed coarse-grained molecular dynamics simulations that successfully predicted the mechanical properties of conjugated polymers and polymer-fullerene composites (Root et al. *Macromolecules* 2016, 49, 2886-2894). In collaboration with Prof. Frederik Krebs at the Danish Technical University, we elucidated the mechanical properties of a large library of >50 low-bandgap semiconducting polymers to determine molecular design rules for maximizing electronic performance with good mechanical deformability (Roth et al. *Chem. Mater.* 2016, 28, 2363-2373). We also determined the effect of cyclic stretching on the microstructure and mechanical properties of conjugated polymers (Printz et al. *Synth. Met.* 2016, 217, 144-151). We used many of these results to produce a new type of ultra-thin, skin-wearable solar cell that could survive many cycles of deformation without degrading significantly (O'Connor et al. *Sol. Energy Mater. Sol. Cells* 2016, 144, 438-444).

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Complementary to the molecular approaches for improving the mechanical robustness of stretchable organic electronics, we also explored the role of encapsulation and adhesion in electronic devices and found that a large increase in stretchability is possible with the use of a stretchable encapsulating layer (Sawyer et al. *Extreme Mech. Lett.* 2016, doi:10.1016/j.eml.2016.03.012). In addition to polymers, we explored the stretchability of semiconducting small molecules, in collaboration with Profs. Quyen Nguyen and Guillermo Bazan (Rodriguez et al. *ACS Appl. Mater. Interfaces* 2016, 8, 11649-11657). We reviewed our results in the context of wearable power sources in an invited book chapter (O'Connor et al. "Soft power: Stretchable and ultra-flexible energy sources for wearable and implantable devices" in *Stretchable Bioelectronics for Medical Devices and Systems*, J.A. Rogers, D.H. Kim, and R. Ghaffari, Eds. Springer, 2016). We also performed an analysis of the interplay and perceived competition between charge-transport and mechanical deformability in organic semiconductors in an invited review (Printz et al. *Appl. Phys. Rev.* 2016, 3, 021302). In an invited perspective article, I described nomenclature and metrology in the field of stretchable electronics (Lipomi *Adv. Mater.* 2016 DOI: 10.1002/adma.201504196).

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Archival Publications (published) during reporting period:

Daniel Rodriguez, Suchol Savagatrup, Eduardo Valle, Christopher M. Proctor, Caitlin McDowell, Guillermo C. Bazan, Thuc-Quyen Nguyen, and Darren J. Lipomi, 2016. Mechanical Properties of Solution-Processed Small-Molecule Semiconductor Films, *ACS Applied Materials & Interfaces*. 8:11649–11657.

Adam D. Printz and Darren J. Lipomi, 2016. Competition between Deformability and Charge Transport in Semiconducting Polymers for Flexible and Stretchable Electronics. *Applied Physics Reviews*, 3:021302.

Timothy F. O'Connor, Suchol Savagatrup, and Darren J. Lipomi, 2015. Soft power: Stretchable and ultra-flexible energy sources for wearable and implantable devices. Chapter in *Stretchable Bioelectronics for Medical Devices and Systems*. Rogers, J. A.; Kim, D.-H.; Ghaffari, R., eds. Springer.

Samuel E. Root, Suchol Savagatrup, Christopher J. Pais, Gaurav Arya, and Darren J. Lipomi, 2016. Predicting the Mechanical Properties of Organic Semiconductors Using Coarse-Grained Molecular Dynamics Simulations. *Macromolecules*, 49:2886-2894.

Adam D. Printz, Andrew S.-C. Chiang, Suchol Savagatrup, and Darren J. Lipomi, 2016. Fatigue in Organic Semiconductors: Spectroscopic Evolution of Microstructure due to Cyclic Loading in Poly(3-Hexylthiophene). *Synthetic Metals*. 217:144-151.

Eric J. Sawyer, Aliaksandr V. Zaretski, Adam D. Printz, Nathaniel V. de los Santos, Alejandra Bautista-Gutierrez, and Darren J. Lipomi, 2016. Large Increase in Stretchability of Organic Electronic Materials by Encapsulation. *Extreme Mechanics Letters*, Available online.

Béranger Roth,† Suchol Savagatrup,† Nathaniel De Los Santos, Ole Hagemann, Jon E. Carlé, Martin Helgesen, Francesco Livi, Eva Bundgaard, Roar R. Søndergaard, Frederik C. Krebs, and Darren J. Lipomi, 2016. Mechanical Properties of a Library of Low-Bandgap Polymers. *Chemistry of Materials* 2016, 28:2363-2373.

Darren J. Lipomi, 2016. Stretchable figures of merit in deformable electronics. *Advanced Materials*. DOI: 10.1002/adma.201504196.

Timothy F. O'Connor, Aliaksandr V. Zaretski, Suchol Savagatrup, Adam D. Printz, Cameron D. Wilkes, Mare I. Diaz, Eric J. Sawyer, Darren J. Lipomi, 2016. Wearable organic solar cells with high cyclic bending stability: Materials selection criteria. *Solar Energy Materials and Solar Cells*. 144:438-444.

Adam D. Printz, Aliaksandr V. Zaretski, Suchol Savagatrup, Andrew S-C. Chiang, and Darren J. Lipomi, 2015. Yield point of semiconducting polymer films on stretchable substrates determined by onset of buckling. *ACS Applied Materials & Interfaces*. 7:23257-23264.

Suchol Savagatrup, Daniel Rodriguez, Adam D. Printz, Alexander B. Sieval, Jan C. Hummelen, and Darren J. Lipomi, 2015. [70]PCBM and incompletely separated grades of methanofullerenes produce bulk heterojunctions with increased robustness for ultra-flexible and stretchable electronics. *Chemistry of Materials*. 27:3902-3911.

Timothy F. O'Connor, Kirtana M. Rajan, Adam D. Printz, and Darren J. Lipomi, 2015. Toward organic electronics with properties inspired by biological tissue. *Journal of Materials Chemistry B*. 3:4947-4952.

Suchol Savagatrup, Adam D. Printz, Haosheng Wu, Kirtana M. Rajan, Eric J. Sawyer, Aliaksandr V. Zaretski, Christopher J. Bettinger, and Darren J. Lipomi, 2015. Viability of stretchable poly(3-heptylthiophene) (P3HpT) for organic solar cells and field-effect transistors. *Synthetic Metals*. 203:208-214.

Aliaksandr V. Zaretski, Herad Moetazedi, Casey Kong, Eric J. Sawyer, Suchol Savagatrup, Eduardo Valle, Timothy F. O'Connor, Adam D. Printz, and Darren J. Lipomi, 2015. Metal-assisted exfoliation (MAE): Green, roll-to-roll compatible method for transferring graphene to flexible substrates. *Nanotechnology*. 26: 045301.

Suchol Savagatrup, Esther Chan, Sandro M. Renteria-Garcia, Adam D. Printz, Aliaksandr V. Zaretski, Timothy F. O'Connor, Daniel Rodriguez, Eduardo Valle, and Darren J. Lipomi, 2015. Plasticization of PEDOT:PSS by common additives for mechanically robust organic solar cells and wearable sensors. *Advanced Functional Materials*. 25:427-436.

Adam D. Printz, Suchol Savagatrup, Daniel Rodriguez, and Darren J. Lipomi, 2015. Role of molecular mixing on the stiffness of polymer:fullerene bulk heterojunction films. *Solar Energy Materials and Solar Cells*. 134:64-72.

Suchol Savagatrup, Adam D. Printz, Timothy F. O'Connor, Aliaksandr V. Zaretski, Daniel Rodriguez, Eric J. Sawyer, Kirtana M. Rajan, Raziell I. Acosta, Samuel E. Root, and Darren J. Lipomi, 2015. Mechanical degradation and stability of organic solar cells: molecular and microstructural determinants. *Energy & Environmental Science*. 8:55-80.

Eric J. Sawyer, Suchol Savagatrup, Timothy F. O'Connor, Aditya S. Makaram, Daniel J. Burke, Aliaksandr V. Zaretski, Adam D. Printz, and Darren J. Lipomi, 2014. Toward intrinsically stretchable organic semiconductors: mechanical properties of high-performance conjugated polymers. *Proc. SPIE*, 9185:91850U-1–91850U-6.

Lisa Chen, Benjamin C-K. Tee, Alex L. Chortos, Gregor Schwartz, Victor Tse, Darren J. Lipomi, H.-S. Philip Wong, Michael V. McConnell, and Zhenan Bao, 2014. Continuous wireless pressure monitoring and

mapping with ultra-small passive sensors for health monitoring and critical care. Nature Communications.
DOI: 10.1038/ncomms6028

Suchol Savagatrup, Adam D. Printz, Timothy F. O'Connor, Aliaksandr V. Zaretski, and Darren J. Lipomi, 2014. Molecularly stretchable electronics. Chemistry of Materials 26:3028-3041 (Invited perpective.)

Suchol Savagatrup, Adam D. Printz, Daniel Rodriquez, and Darren J. Lipomi, 2014. Best of both worlds: Conjugated polymers exhibiting good photovoltaic properties and high tensile elasticity. Macromolecules, 47:1981-1992.

Adam D. Printz, Suchol Savagatrup, Daniel J. Burke, Trevor N. Purdy, and Darren J. Lipomi, 2014. Increased elasticity of a low-bandgap semiconducting polymer by random segmentation for mechanically robust solar cells. RSC Advances, 4:13635-13643.

Suchol Savagatrup, Aditya S. Makaram, Daniel J. Burke, and Darren J. Lipomi, 2014. Mechanical properties of conjugated polymers and polymer-fullerene composites as a function of molecular structure. Advanced Functional Materials, 24:1169–1181.

Timothy F. O'Connor, Aliaksandr V. Zaretski, Bijan A. Shiravi, Suchol Savagatrup, Adam D. Printz, Mare Ivana Diaz, and Darren J. Lipomi, 2014. Stretching and conformal bonding of organic solar cells to hemispherical substrates. Energy & Environmental Science, 7:370–378.

Daniel J. Burke and Darren J. Lipomi, 2013. Green chemistry for organic solar cells. Energy & Environmental Science, 6:2053–2066.

18. New discoveries, inventions, or patent disclosures:

Do you have any discoveries, inventions, or patent disclosures to report for this period?

Please describe and include any notable dates

Do you plan to pursue a claim for personal or organizational intellectual property?

Changes in research objectives (if any):

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Extensions granted or milestones slipped, if any:

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Reporting Period

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Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, \$K)

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